

Using Molecular Simulation to Compute Transport Coefficients of Molecular Gases

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Abstract

The existing kinetic theory of gases is based on an analytical approach that becomes intractable for all but the simplest molecules.

Here we propose a simple numerical scheme to compute the transport properties of molecular gases in the limit of infinite dilution. The approach that we propose is approximate, but our results for the diffusivity D , the viscosity η and the thermal conductivity λ of hard spheres, Lennard-Jones particles and rough hard spheres, agree well with the standard (lowest order) Chapman-Enskog results. We also present results for a Lennard-Jones-dimer model for nitrogen, for which no analytical results are available. In the case of poly-atomic molecules (we consider n-octane), our method remains simple and gives good predictions for the diffusivity and the viscosity. Computing the thermal conductivity of poly-atomic molecules requires an approximate treatment of their quantized internal modes. We show that a well-known approximation that relates λ to D and η , yields good results. We note that our approach should yield a lower limit to the exact value of D , η and λ . Interestingly, the most sophisticated (higher-order) Chapman-Enskog results for rough hard spheres seem to violate this bound.

Introduction

The theoretical framework for computing the transport coefficients of gases was developed by Boltzmann in 1872¹. General methods to compute the transport coefficients for spherical particles were developed by Chapman and Enskog, just over a century ago (see e.g. ref. 2). At that time (almost half a century before the advent of computer simulations) the focus was on obtaining analytical expressions for certain classes of pair potentials. However, the more general case of molecules with internal degrees of freedom cannot be solved with such an analytical approach, except in a small number of very simple, or highly simplified cases. Strangely, this state of affairs has barely changed during the past half century. One

reason may be that the Chapman-Enskog formalism is not for the faint-hearted: as Chapman himself (quoted in the Observer of July 7, 1957, p11), said about his book²): *It is very-heavy going and “like chewing glass”*.

The apparent lack of simulation-based studies of molecular transport properties is all the more surprising as there are literally thousands of papers on molecular trajectory calculations (a review from 1974 already lists 245 references³), many of them aimed at studying molecular scattering and collision-induced relaxation of intra-molecular degrees of freedom. Yet, most of these thousands of papers do not aim to compute transport properties. Notable exceptions are the papers by Nyeland et al.⁴ on the transport properties of gaseous nitrogen, and the paper by Viehland et al.⁵ on the mobility of NO^+ in Helium. Whilst there are a few other papers reporting similar calculations, we have been unable to find systematic molecular-trajectory calculations of the transport properties of molecular gases containing more than 2 atoms. The lack of such papers is not surprising, as the calculations are far from simple (as mentioned explicitly in ref. 5).

Surprisingly, the situation is better for liquids than for gases because the advent of Molecular Dynamics simulations made it possible to compute a variety of transport coefficients as integrals of time correlation functions, using the so-called Green-Kubo relations (see e.g. 6). However, this did not help the problem of transport in gases at low densities, as the relevant time-correlation functions decay increasingly slowly as the density is decreased, and as a consequence the statistical error in the transport coefficients diverges as the density tends to zero⁷. As a consequence, the number of Molecular Dynamics calculations of transport coefficients of dilute gases is very small. An MD study by Lee and Kim of the the transport coefficients of simple diatomic gases at atmospheric pressure⁸ provides an illustration of the technical challenges of a “brute force” MD approach: these simulations are reasonably long ($\mathcal{O}(10)$ ns), yet 10 ns corresponds to only $\mathcal{O}(50)$ correlation times. Hence, the statistical error in the transport coefficients (except the diffusivity) is expected to be appreciable (although a non-standard analysis may mitigate the problems somewhat⁹).

Summarizing this discussion: there seems to be no efficient, generally applicable method to compute the transport coefficients of dilute poly-atomic, molecular gases for which Chapman-Enskog-style analytical approaches become intractable. This is a real problem, as knowledge of the transport coefficients of dilute gases is important in many fields, such as atmospheric science. The aim of the present paper is to fill this gap. We consider the calculation of the most important transport coefficients of a pure gas of molecules with finite ranged, but otherwise arbitrary, intermolecular potentials. As we show, these expressions lend themselves to simple numerical simulations.

Green-Kubo relations

Rather than starting from the Boltzmann equation, we start from the Green-Kubo (GK) expressions (see e.g. 6) for the most important transport coefficients: the diffusivity D , the shear viscosity η and the thermal conductivity λ . The GK relations relate the various transport to an integral of the time auto-correlation function of the appropriate flux, as listed below.

$$D = \frac{1}{3} \int_0^\infty d\tau \langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \rangle = \int_0^\infty d\tau \langle v^x(\tau) v^x(0) \rangle \quad (1)$$

The Green-Kubo relation for the shear viscosity η is:

$$\eta = \frac{1}{Vk_B T} \int_0^\infty dt \langle \sigma^{xy}(0) \sigma^{xy}(t) \rangle \quad (2)$$

with

$$\sigma^{xy} = \sum_{i=1}^N \left(m_i v_i^x v_i^y + \frac{1}{2} \sum_{j \neq i} x_{ij} f_y(r_{ij}) \right); \quad (3)$$

Finally, the thermal conductivity λ , can be obtained from

$$\lambda = \frac{1}{Vk_B T^2} \int_0^\infty dt \langle j_z^Q(0) j_z^Q(t) \rangle \quad (4)$$

where the heat flux j_z^Q is given by

$$j_z^Q = \frac{d}{dt} \sum_{i=1}^N z_i \left[\left(\frac{1}{2} m_i v_i^2 + E_{\text{int}}^{(i)} - h_i \right) + \sum_{j \neq i} v(r_{ij}) \right], \quad (5)$$

where $E_{\text{int}}^{(i)}$ is the internal (vibration, rotation, electronic) energy of molecule i and h_i is its the average enthalpy ($h_i = \frac{5}{2} k_B T + \langle E_{\text{int}}^{(i)} \rangle$). These expressions are generally valid for pairwise additive potentials, and are used extensively in Molecular Dynamics simulations to compute the transport coefficients of dense fluids. However, in the dilute gas limit, the GK integrals – although still correct – converge slowly, and the statistics become poor. The problem is analogous to computing the second virial coefficient B_2 in simulation: yes, it would be possible to compute B_2 by evaluation the compressibility factor of a dilute gas, but the method does not work well, and direct computation of the explicit expression for B_2 is preferable. The same holds for transport coefficients of dilute gases.

Green-Kubo relations for dilute gases

In dilute gases, the GK expressions for η and λ simplify, because we can ignore the contribution to the fluxes due to terms involving the intermolecular interactions. That is:

$$\sigma^{xy} = \sum_{i=1}^N m_i v_i^x v_i^y \quad (6)$$

and

$$j_z^Q = \sum_{i=1}^N \hat{\mathbf{z}} \cdot \mathbf{v}_i \left[\frac{1}{2} m_i v_i^2 + E_{\text{int}}^{(i)} - h_i \right] \quad (7)$$

The expression for the diffusion coefficient remains unchanged. It is worth pointing out that, when using the Green-Kubo expression for one-component fluids, the constant h_i is usually omitted. However, this is only allowed if we can work in a reference frame where $\sum_i \mathbf{v}_i = 0$. But later on, when we compute the heat flux correlation function by considering independent binary collisions, there is no such cancellation on a term-by-term basis: hence the h_i should

be retained.

The next simplification comes from the fact that, in very dilute gases, the “molecular chaos” assumption holds: molecules undergo infrequent collision events with a typical duration τ_c separated by time intervals between collisions of order τ_{bc} , such that $\tau_{bc} \gg \tau_c$. For molecules with attractive interactions, a small fraction of all collisions (“orbiting collisions”) may take arbitrarily long, making the time-scale separation between τ_{bc} and τ_c questionable. The simulation time limits the largest values of τ_c that can be probed. Note that we can ignore true bound states that can only be broken up by a collision with a third particle, as the concentration of bound pairs vanishes quadratically at low densities.

The molecular chaos assumption implies that successive collision events are uncorrelated. In the low-density limit, this hypothesis is justified (at higher densities mode-coupling effects become important and the molecular chaos approximation breaks down).

BGK approximation

We now make an important additional assumption, namely that the relevant correlation functions decay as single exponentials. This is *not* correct, not even at infinite dilution. In the context of the solution of the Boltzmann equation, the “single-exponential” approximation is usually referred to as the BGK (Bhatnagar, Gross and Krook¹⁰) approximation. Strictly speaking, we do not have to use a BGK-like approximation, but if we do not, the present scheme loses much of its simplicity. In what follows, we shall refer to the “single-exponential” approximation, as the BGK approximation.

One more comment is in order: The range of interaction between molecules is typically not finite, hence strictly-speaking, the duration of a collision is not finite. Whilst this is true, we should expect that in many cases of practical importance, the transport properties of particles with a finite interaction range r_c will approach those of particles with the full interaction, provided we choose r_c large enough. In what follows, we will therefore always assume that the inter-particle interactions have a finite range r_c . We stress that such an

approach will not work for molecules interacting through long-ranged interactions. However, extension of our numerical method to systems with true long-ranged interactions between uncharged molecules, is straightforward. Such an extension is achieved by a change of variables in the collision integrals (see SI).

Let us next consider the three correlation functions mentioned above. We denote these correlation functions by $C_\alpha(t)$, where α may refer to the velocity, stress or heat flux. It should be emphasised that the velocity is a single-particle property and hence it is only necessary to follow the effect of a collision on one of the two collision partners. However, stress and heat flux are collective properties, hence we have to compute how a collision changes the stress or heat flux of a *pair* of particles. In the regime where molecular chaos holds, we can write (within the BGK approximation):

$$C_\alpha(t) = \langle J_\alpha^2 \rangle e^{-t/\tau_\alpha}, \quad (8)$$

where J_α denotes the flux associated with α , and hence

$$\int_0^\infty dt C_\alpha(t) = \langle J_\alpha^2 \rangle \tau_\alpha \quad (9)$$

Our aim is therefore to compute τ (for dilute gases the equilibrium average $\langle J_\alpha^2 \rangle$ can be evaluated analytically – or almost analytically, in the case of heat fluxes of particles with internal degrees of freedom). To obtain an expression for τ , we note that

$$\left(\frac{\partial C_\alpha(t)}{\partial t} \right)_{t=0+} = - \frac{\langle J_\alpha^2 \rangle}{\tau_\alpha} \quad (10)$$

Hence,

$$\int_0^\infty dt C_\alpha(t) = - \langle J_\alpha^2 \rangle \left(\frac{\langle J_\alpha^2 \rangle}{\dot{C}_\alpha(0+)} \right) \quad (11)$$

Note that the decay of $C_\alpha(t)$ is due to the (uncorrelated) collision events. We can therefore

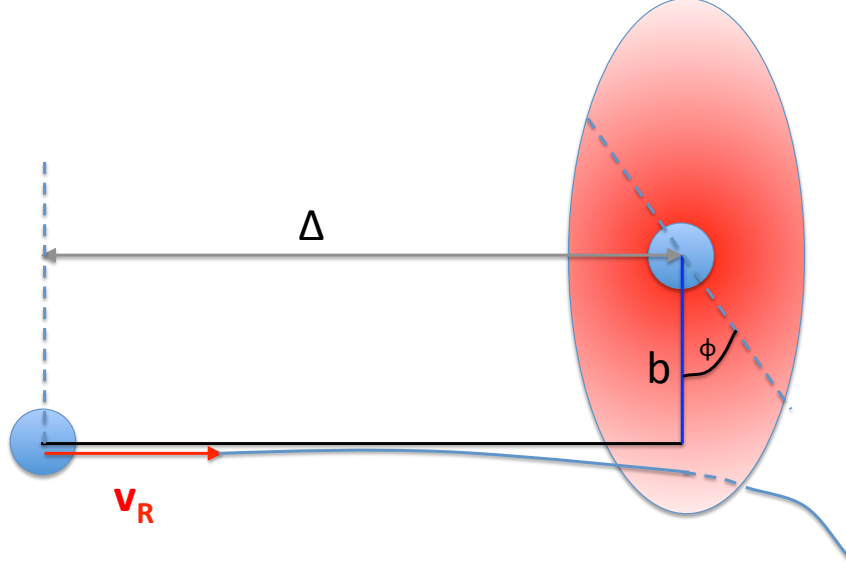


Figure 1: Sketch of the collision geometry of two particle with relative velocity v_{rel} and impact parameter b . If the particles are not spherically symmetric, we should average over all particle orientations: in that case, the angle ϕ is unimportant and can be taken equal to 0.

write $\dot{C}_\alpha(0+)$ as

$$\dot{C}_\alpha(0+) = \langle J_\alpha \Delta_c J_\alpha \rangle_c \times \Gamma_c \quad (12)$$

where $\Delta_c J_\alpha$ denotes the change in J_α in a single collision, $\langle \dots \rangle_c$ denotes averaging over all collision conditions (see below), and Γ_c is the collision frequency. The number of collisions experienced per unit time by a single particle is equal to $\Gamma^{(1)} = \rho \pi r_c^2 \langle v_{\text{rel}} \rangle$, where ρ is the number density and r_c is the maximum range of the interaction between collision partners¹, and v_{rel} is the relative velocity of two collision partners. The total collision frequency of N particles is $\Gamma^{(N)} = (N/2)\Gamma^{(1)}$. The factor 1/2 is needed because every collision involves *two*

¹In fact, the collision cross section may be chosen larger than πr_c^2 , because this factor drops out of the overall expression. However, a smaller collision cross section than πr_c^2 is not allowed.

particles.

In the case of diffusion, J_α is the velocity of a single particle in (say) the x -direction, and hence

$$\dot{C}_D(0+) = \langle v_x \Delta_c v_x \rangle_c \times \Gamma^{(1)} . \quad (13)$$

However, in the case of viscosity and heat conductivity, J_α is an N -particle current. Yet, when we consider $\langle J_\alpha \Delta_c J_\alpha \rangle_c$, only the terms in J_α due to the collision partners are correlated with $\Delta_c J_\alpha$, which involves those particles. In what follows, we will denote that part of the current that is changed in a collision by j_α .

Let us consider the variation of $C_\alpha(t)$ in the interval $0 \leq t \leq t^*$, where t^* is a time interval much larger than the duration of a collision, but much shorter than the average time between collisions experienced by a typical particle. We define $\Delta c_\alpha(t^*)$, the average change of $J_\alpha(0)J_\alpha(t)$ due to a *single* collision event. As mentioned above, a single collision will only affect the flux due to one (diffusion) or two (η or λ) particles. Using our definition for j_α , we can then write:

$$\Delta(j_\alpha(0)j_\alpha(t^*)) = j_\alpha(0) (j_\alpha(t^*) - j_\alpha(0)) = j_\alpha(0)\Delta j_\alpha(t^*) \quad (14)$$

where the last equality defines $\Delta j_\alpha(t^*)$

$$\Delta j_\alpha(t^*) \equiv j_\alpha(t^*) - j_\alpha(0) . \quad (15)$$

To obtain \dot{C}_α , we have to consider all collision conditions (relative speed, impact parameter, internal energy) and take an average.

The rate of change of $\langle j_\alpha(0)\Delta j_\alpha(t^*) \rangle$ is equal to the average change in $j_\alpha(0)j_\alpha(t^*)$ during an interval of length t^* . This can be written as the average change in $j_\alpha(0)j_\alpha(t^*)$ during a collision, multiplied by the number of collisions per time interval t^* . We define a collision as any event where two particles that were initially not interacting cross through each other's

interaction zone. For particles with a relative velocity v_{rel} , the number of such events, in an interval t^* is $\rho t^* v_{\text{rel}} \pi r_c^2$ (i.e. the number of particles in a cylinder with cross-section πr_c^2 and height $t^* v_{\text{rel}}$). Note that it is convenient to use a coordinate system where one axis (say X) is along the direction of the relative velocity of the collision pair. It is important to distinguish between the lab-based coordinate frame x, y, z and the collision frame X, Y, Z . Later we will have to average over all orientations of X, Y, Z with respect to the lab frame. The distribution of the magnitude of the relative velocity is

$$P(v_{\text{rel}}) = 4\pi \left(\frac{\beta\mu}{2\pi} \right)^{3/2} v_{\text{rel}}^2 \exp\left(-\frac{1}{2}\beta\mu v_{\text{rel}}^2\right), \quad (16)$$

where $\mu \equiv m_1 m_2 / (m_1 + m_2)$ is the reduced mass of particles with masses m_1 and m_2 . In this coordinate frame (see Fig. 1), we initially position the two collision partners at a distance Δ in the direction of \mathbf{v}_{rel} , whilst the distance in the perpendicular direction is given by the (2D) polar coordinates b and ϕ . The value of $\Delta j_\alpha(t^*)$ depends both on the value of v_{rel} and on the “impact parameter” b , i.e. the magnitude of the projection of the initial inter-particle distance of the plane perpendicular to v_{rel} .

Our aim is to compute the rate of change of $\langle j_\alpha(0) \Delta j_\alpha(t^*) \rangle$ due to single collision events. The averaging is done over all impact parameters and over all relative velocities (and, in the heat flux case, over all center-of-mass speeds):

$$\begin{aligned} \dot{c}_\alpha &= \rho \langle j_\alpha(0) \Delta j_{\alpha;c} \rangle_1 \\ &= \rho \int dX_{\text{int}} P(X_{\text{int}}) \int_0^{r_c} \pi db^2 \int_0^\infty dv_{\text{rel}} v_{\text{rel}} P(v_{\text{rel}}) j_\alpha(0) \Delta j_{\alpha;c}(b, v_{\text{rel}}; X_{\text{int}}), \end{aligned} \quad (17)$$

where $\Delta j_{\alpha;c}(b, v_{\text{rel}}; X_{\text{int}})$ denotes the change in j_α during one collision with impact parameter b and relative velocity v_{rel} , given that the initial state of the collision pair is given by X_{int} : X_{int} is used to denote all the internal degrees of freedom of both particles *before* the collision, *and* the center-of-mass velocity of the collision pair (as we shall see below, this quantity is only important for the thermal conductivity).

Note that

$$\Gamma^{(1)} = \rho \pi r_c^2 \langle v_{\text{rel}} \rangle = \rho \int dX_{\text{int}} P(X_{\text{int}}) \int_0^{r_c} \pi db^2 \int_0^\infty dv_{\text{rel}} v_{\text{rel}} P(v_{\text{rel}}) \quad (18)$$

We can therefore rewrite Eqn. 17 as

$$\begin{aligned} \dot{c}_\alpha &= \Gamma^{(1)} \frac{\int dX_{\text{int}} P(X_{\text{int}}) \int_0^{r_c} \pi db^2 \int_0^\infty dv_{\text{rel}} v_{\text{rel}} P(v_{\text{rel}}) j_\alpha(0) \Delta j_{\alpha;c}(b, v_{\text{rel}}; X_{\text{int}})}{\langle v_{\text{rel}} \rangle \pi r_c^2} \\ &\equiv \Gamma^{(1)} \langle j_\alpha(0) \Delta j_\alpha \rangle_c . \end{aligned} \quad (19)$$

Eqn. 19 is convenient because it expresses \dot{c}_α as the product of a collision frequency and an average contribution per collision.

For convenience, we have assumed that the interaction potential has a finite range r_c , such that we can limit the integration over impact parameters to values less than r_c .

It is important to note that $j_\alpha(0)$ refers to the state *before* the collision particles interact, and $\Delta j_{\alpha;c}$ denotes the difference between $j_\alpha(0)$ and the value of j_α *after* the collision. Hence, neither $j_\alpha(0)$ nor $\Delta j_{\alpha;c}$ depend explicitly on time. More importantly, $j_\alpha(0)$ and $\Delta j_{\alpha;c}$ contain only kinetic contributions (*e.g.* v^x or $v^x v^y$) and no inter-molecular interaction terms.

The next step is to separate the particle velocities in a center-of-mass part and the relative velocity:

$$\mathbf{v}^{(1)} = \mathbf{v}_{\text{CM}} + \frac{m_2}{m_1 + m_2} \mathbf{v}_{\text{rel}} , \quad (20)$$

and

$$\mathbf{v}^{(2)} = \mathbf{v}_{\text{CM}} - \frac{m_1}{m_1 + m_2} \mathbf{v}_{\text{rel}} , \quad (21)$$

where

$$\mathbf{v}_{\text{CM}} \equiv \frac{m_1 \mathbf{v}_{\text{rel}}^{(1)} + m_2 \mathbf{v}_{\text{rel}}^{(2)}}{m_1 + m_2} , \quad (22)$$

and

$$\mathbf{v}_{\text{rel}} \equiv \mathbf{v}_{\text{rel}}^{(1)} - \mathbf{v}_{\text{rel}}^{(2)} . \quad (23)$$

We can always decompose j_α in j_α^{CM} and j_α^{rel} . Importantly, j_α^{CM} is unchanged in a collision, and $\Delta j_{\alpha;c}$ is independent of $j_\alpha^{\text{CM}}(0)$ ². Hence

$$\dot{c}_\alpha = \int dX_{\text{int}} P(X_{\text{int}}) \int_0^{r_c} \pi db^2 \int d\mathbf{v}_{\text{CM}} P(\mathbf{v}_{\text{CM}}) \int_0^\infty dv_{\text{rel}} (\rho v_{\text{rel}}) P(v_{\text{rel}}) j_\alpha(0) \Delta j_{\alpha_c} , \quad (24)$$

The center-of-mass velocity still shows up in this equation, but this dependence is only needed for the heat conductivity. In what follows, we will assume for simplicity that we are considering a pure substance. In that case $m_1 = m_2 \equiv m$. Let us now consider the expressions for D , η and λ using x, y, z to denote directions in the lab frame. In the case of diffusion, we have

$$j_D = v^x \quad (25)$$

For η we have

$$j_\eta = m \sum_{i=1}^2 v_i^x v_i^y \quad (26)$$

and for λ

$$j_\lambda = \sum_{i=1}^2 v_i^x \left(\frac{1}{2} m v_i^2 + E_{\text{int}}^{(i)} - h_i \right) , \quad (27)$$

where $E_{\text{int}}^{(i)}$ denotes the total (kinetic plus potential) internal energy of molecule i . The internal energy comprises rotational and vibrational (and possibly electronic) contributions. Note that for η and λ , the corresponding expression for α contains the contribution of both collision partners.

For \dot{C}_D , we can now write:

$$\dot{c}_D = \frac{\rho \Gamma^{(1)}}{4} \langle v_{\text{rel}}^x \Delta v_{\text{rel}}^x \rangle_c . \quad (28)$$

The factor $(1/4)$ in front of Eqn. 28 is due to the fact the velocity of a *single* particle is $\mathbf{v}_{\text{CM}} \pm (1/2)\mathbf{v}_{\text{rel}}$. \dot{c}_D does not depend on \mathbf{v}_{CM} , but the factor $\pm(1/2)$ in front of \mathbf{v}_{rel} enters

²As we shall when discussing the heat flux, it is a bit more subtle: $\Delta j_{\alpha;c}$ may still depend on the magnitude of \mathbf{v}_{CM} , but not on its orientation.

quadratically in Eqn. 28. When we average the orientations of the collision frame with respect to the lab frame, we can write

$$v_{\text{rel}}^x(\Delta v_{\text{rel}}^x) = \frac{1}{3} v_{\text{rel}}(0) [v_{\text{rel}}(1) \cos \theta - v_{\text{rel}}(0)] , \quad (29)$$

where we have averaged over all orientations of v_x in the lab frame. We have defined

$$\cos \theta \equiv \hat{\mathbf{v}}_{\text{rel}}(0) \cdot \hat{\mathbf{v}}_{\text{rel}}(1) , \quad (30)$$

and $v_{\text{rel}}(0)$, $v_{\text{rel}}(1)$ denote the relative velocities before and after the collision. In eqn. 28, the dependence on \mathbf{v}_{CM} has disappeared because during a collision $\Delta \mathbf{v}_{\text{CM}} = 0$ and, in addition, $\mathbf{v}_{\text{CM}}(0)$ is not correlated with $\Delta \mathbf{v}_{\text{rel}}$. Note that we have assumed that \mathbf{v}_{rel} is initially in the $+x$ direction. Although the internal degrees of freedom do not enter explicitly in the expression for \dot{c}_D , they enter implicitly, because they may affect the post-collisional relative velocity. This is different for particles with no internal degrees of freedom: in that case all collisions are elastic, and the magnitude of the relative velocity is not changed by the collision. From Eqns. 28 and 29 it follows that

$$\dot{c}_D = \frac{\Gamma^{(1)}}{12} \langle v_{\text{rel}}(0) [v_{\text{rel}}(1) \cos \theta - v_{\text{rel}}(0)] \rangle_c , \quad (31)$$

For η we have

$$\dot{c}_\eta = \frac{\rho m^2}{4} \langle v_{\text{rel}}^x v_{\text{rel}}^y (\Delta v_{\text{rel}}^x v_{\text{rel}}^y) \rangle_c , \quad (32)$$

For the viscosity η and the thermal conductivity λ , the distinction between \dot{C}_α and \dot{c}_α is important: $\dot{C}_\eta = (N/2)\dot{c}_\eta$ and $\dot{C}_\lambda = (N/2)\dot{c}_\lambda$.

The expression in Eqn. 32 does not depend on \mathbf{v}_{CM} because a) in the 2-particle stress $\sum_{i=1}^2 v_i^x v_i^y$, all cross terms between \mathbf{v}_{CM} and \mathbf{v}_{rel} cancel b) the center-of-mass contribution to the stress is conserved during a collision and c) upon averaging over all directions of \mathbf{v}_{CM} , the cross-correlation between $v_{\text{CM}}^x v_{\text{CM}}^y$ and $\Delta v_{\text{rel}}^x v_{\text{rel}}^y$ vanishes. When we average over

all orientations of X, Y, Z with respect to x, y, z we get (see SI):

$$v_{\text{rel}}^x v_{\text{rel}}^y (\Delta v_{\text{rel}}^x v_{\text{rel}}^y) = \frac{1}{15} v_{\text{rel}}^2(0) (v_{\text{rel}}^2(1) P_2(\cos \theta) - v_{\text{rel}}^2(0)) . \quad (33)$$

We can then rewrite \dot{c}_η as

$$\dot{c}_\eta = \frac{\Gamma m^2}{60} \langle v_{\text{rel}}^2(0) (v_{\text{rel}}^2(1) P_2(\cos \theta) - v_{\text{rel}}^2(0)) \rangle_c . \quad (34)$$

Finally, for the heat flux, we obtain:

$$\dot{c}_\lambda = \Gamma^{(1)} \left\langle \sum_{i=1}^2 v_i^x \left(\frac{1}{2} m v_i^2 + E_{\text{int}}^{(i)} - h_i \right) \Delta \left[\sum_{i=1}^2 v_i^x \left(\frac{1}{2} m v_i^2 + E_{\text{int}}^{(i)} - h_i \right) \right] \right\rangle_c . \quad (35)$$

Eqn. 35 for heat transport needs further simplification. Let us focus on the heat flux itself

$$\sum_{i=1}^2 v_i^x \left(\frac{1}{2} m v_i^2 + E_{\text{int}}^{(i)} - h_i \right) = v_{\text{CM}}^x (E_{\text{tot}}^{1,2} - 2h) + \frac{1}{2} v_{\text{rel}}^x (E^{(1)} - E^{(2)}) , \quad (36)$$

where $E_{\text{tot}}^{1,2}$ denotes the total energy of the collision pair (1,2), and $E^{(i)}$ denotes the energy of collision partner i . Note that in the second half of this expression, the average enthalpy has dropped out as it does not change during the collision. Moreover, as $E_{\text{tot}}^{1,2}$ is conserved during a collision, we only need to consider the change during the collision of the second term (involving $E^{(1)} - E^{(2)}$). As the directions of \mathbf{v}_{CM} and \mathbf{v}_{rel} are uncorrelated, there is no cross correlation between the terms involving $\hat{\mathbf{v}}_{\text{CM}}$ before the collision and the one involving $\hat{\mathbf{v}}_{\text{rel}}$ after the collision. Here $\hat{\mathbf{a}}$ denotes the unit vector in direction of \mathbf{a} . However, even though all vectorial correlations between \mathbf{v}_{CM} and \mathbf{v}_{rel} vanish, we will still find scalar correlations.

The terms that we need to consider are of the form

$$\left[\frac{1}{2} v_{\text{rel}}^x \left(\frac{1}{2} m v_1^2 - \frac{1}{2} m v_2^2 + E_{\text{int}}^{(1)} - E_{\text{int}}^{(2)} \right) \right] . \quad (37)$$

As

$$\frac{1}{2}mv_1^2 - \frac{1}{2}mv_2^2 = m\mathbf{v}_{\text{CM}} \cdot \mathbf{v}_{\text{rel}} \quad (38)$$

we must compute

$$\begin{aligned} & \frac{1}{2}v_{\text{rel}}^x(0) \left[m\mathbf{v}_{\text{CM}} \cdot \mathbf{v}_{\text{rel}}(0) + E_{\text{int}}^{(1)}(0) - E_{\text{int}}^{(2)}(0) \right] \\ & \times \frac{1}{2}v_{\text{rel}}^x(0) \left[m\mathbf{v}_{\text{CM}} \cdot \mathbf{v}_{\text{rel}}(0) + E_{\text{int}}^{(1)}(0) - E_{\text{int}}^{(2)}(0) \right] \end{aligned}$$

and

$$\begin{aligned} & \frac{1}{2}v_{\text{rel}}^x(0) \left[m\mathbf{v}_{\text{CM}} \cdot \mathbf{v}_{\text{rel}}(0) + E_{\text{int}}^{(1)}(0) - E_{\text{int}}^{(2)}(0) \right] \\ & \times \frac{1}{2}v_{\text{rel}}^x(1) \left[m\mathbf{v}_{\text{CM}} \cdot \mathbf{v}_{\text{rel}}(1) + E_{\text{int}}^{(1)}(1) - E_{\text{int}}^{(2)}(1) \right] , \end{aligned}$$

where the arguments (0) and (1) denote the states before and after the collision respectively.

The important point to note is that these expressions still depend of \mathbf{v}_{CM} . However, terms linear in \mathbf{v}_{CM} will vanish upon averaging over orientations. We first average

$$\begin{aligned} & \frac{1}{2}v_{\text{rel}}^x(0) [m\mathbf{v}_{\text{CM}} \cdot \mathbf{v}_{\text{rel}}(0)] \\ & \times \frac{1}{2}v_{\text{rel}}^x(0) [m\mathbf{v}_{\text{CM}} \cdot \mathbf{v}_{\text{rel}}(0)] \end{aligned}$$

over a Maxwell distribution of \mathbf{v}_{CM} :

$$\frac{1}{3} \frac{m^2}{4} v_{\text{rel}}^2(0) \langle [\mathbf{v}_{\text{CM}} \cdot \mathbf{v}_{\text{rel}}(0)]^2 \rangle_{V_{\text{CM}}} = \frac{m^2}{12} v_{\text{rel}}^2(0) v_{\text{rel}}^2(0) \frac{k_B T}{2m} = \frac{mk_B T}{24} v_{\text{rel}}^4(0) \quad (39)$$

Similarly

$$\frac{m^2}{12} \mathbf{v}_{\text{rel}}(0) \cdot \mathbf{v}_{\text{rel}}(1) \langle [\mathbf{v}_{\text{CM}} \cdot \mathbf{v}_{\text{rel}}(0)][\mathbf{v}_{\text{CM}} \cdot \mathbf{v}_{\text{rel}}(1)] \rangle_{V_{\text{CM}}} = \frac{mk_B T}{24} v_{\text{rel}}^2(0) v_{\text{rel}}^2(1) \cos^2 \theta . \quad (40)$$

The above result follows (for instance) from the spherical-harmonics addition theorem.

Hence, gathering all terms, we get

$$\begin{aligned}
j_\lambda(0)\Delta j_\lambda &\equiv \sum_{i=1}^2 v_i^x \left(\frac{1}{2} m v_i^2 + E_{\text{int}}^{(i)} \right) \Delta \left[\sum_{i=1}^2 v_i^x \left(\frac{1}{2} m v_i^2 + E_{\text{int}}^{(i)} \right) \right] \\
&= \frac{1}{12} \left[-v_{\text{rel}}^2(0) [E_{\text{int}}^{(1)}(0) - E_{\text{int}}^{(2)}(0)]^2 \right. \\
&\quad + v_{\text{rel}}(0) v_{\text{rel}}(1) \cos \theta [E_{\text{int}}^{(1)}(0) - E_{\text{int}}^{(2)}(0)] [E_{\text{int}}^{(1)}(1) - E_{\text{int}}^{(2)}(1)] \\
&\quad \left. + \frac{m k_B T}{2} v_{\text{rel}}^2(0) [v_{\text{rel}}^2(1) \cos^2 \theta - v_{\text{rel}}^2(0)] \right] \tag{41}
\end{aligned}$$

which can be written as

$$\begin{aligned}
\dot{c}_\lambda &= \frac{\Gamma}{12} \left[\left\langle -v_{\text{rel}}^2(0) [E_{\text{int}}^{(1)}(0) - E_{\text{int}}^{(2)}(0)]^2 \right\rangle_c \right. \\
&\quad + \left\langle v_{\text{rel}}(0) v_{\text{rel}}(1) \cos \theta [E_{\text{int}}^{(1)}(0) - E_{\text{int}}^{(2)}(0)] [E_{\text{int}}^{(1)}(1) - E_{\text{int}}^{(2)}(1)] \right\rangle_c \\
&\quad \left. + \left\langle \frac{m k_B T}{2} v_{\text{rel}}^2(0) [v_{\text{rel}}^2(1) \cos^2 \theta - v_{\text{rel}}^2(0)] \right\rangle_c \right] \tag{42}
\end{aligned}$$

Returning now to the Green-Kubo expressions,

$$\int_0^\infty dt C_\alpha(t) = - \langle j_\alpha^2 \rangle \left(\frac{\langle j_\alpha^2 \rangle}{\dot{C}_\alpha(0+)} \right), \tag{43}$$

we need to evaluate in the case of diffusion:

$$- \langle v^2 \rangle \left(\frac{\langle v^2 \rangle}{\dot{C}_D(0+)} \right), \tag{44}$$

and

$$\int_0^\infty dt C_D(t) = - \langle v^2 \rangle \left(\frac{\langle v^2 \rangle}{\dot{C}_D(0+)} \right), \tag{45}$$

For η and λ we also first need expressions for $\langle j_\alpha^2 \rangle / \dot{C}_\alpha(0+)$.

Below we give these expressions for D , η and λ :

For D :

$$\frac{\langle v_x^2 \rangle^2}{\dot{C}_D(0+)} = \frac{(k_B T / m)^2}{\dot{C}_D(0+)} \tag{46}$$

where $\dot{C}_D(0+)$ is given by Eqn. 28.

For η :

$$\frac{\langle (mv_x v_y)^2 \rangle}{\dot{c}_\eta(0+)} = \frac{(k_B T)^2}{\dot{c}_\eta(0+)} \quad (47)$$

For λ :

$$\begin{aligned} & \frac{\langle [v_x((1/2)mv^2 + (E_{\text{int}} - h))]^2 \rangle}{\dot{c}_\lambda(0+)} \\ &= \frac{k_B T}{m} \frac{[\langle (E_{\text{int}} - h)^2 \rangle + 5 \langle (E_{\text{int}} - h) \rangle k_B T + (35/4)(k_B T)^2]}{\dot{c}_\lambda(0+)} \\ &= \frac{k_B T}{m} \frac{[k_B T^2 C_V^{\text{int}} + 5/2(k_B T)^2]}{\dot{c}_\lambda(0+)} \end{aligned} \quad (48)$$

where we have use the fact that $h = E_{\text{int}} + (5/2)k_B T$ and $\langle (E_{\text{int}} - \langle E_{\text{int}} \rangle)^2 \rangle = k_B T^2 C_V^{\text{int}}$.

To obtain the expressions for the transport properties, we must correct for the fact that, for the stress and the heat flux (but not for the self-diffusion), \dot{c}_α refers to the change in the current due to *two* particles. The final expressions are then:

$$D = -\frac{(k_B T/m)^2}{\dot{C}_D(0+)} \quad (49)$$

$$\eta = -2\rho k_B T \frac{(k_B T)^2}{\dot{c}_\eta(0+)} \quad (50)$$

$$\begin{aligned} \lambda &= -\frac{2\rho}{k_B T^2} \left(\frac{k_B T}{m} \right)^2 \\ &\times \frac{[k_B T^2 C_V^{\text{int}} + 5/2(k_B T)^2]^2}{\dot{c}_\lambda(0+)} \end{aligned} \quad (51)$$

In what follows, we focus on these three transport properties, although others can be computed as well. Examples are given in the SI.

Slowly relaxing internal degrees of freedom

As is clear from Eqns. 35 and ?? (but implicitly also from the expressions for the other transport properties) energy exchange with internal degrees of freedom affects the transport properties. If these degrees of freedom can be described by classical mechanics, there is no need for additional discussion, unless they are weakly coupled to the collision dynamics. However, for polyatomic molecules, many vibrational modes will have frequencies ν such that the thermal energy $k_B T$ is (much) less than $h\nu$ (where h is Planck's constant). There are two reasons why such modes should not be described by classical mechanics: first of all, the heat capacity of quantized modes is less than the corresponding classical value, and secondly, it would be incorrect to describe the collision dynamics of quantum modes with classical mechanics. Nevertheless, to a good approximation we can still use the framework described above, provided that the “hard” (e.g. quantized) modes relax slowly. We can then make the approximation that the energy stored in these internal degrees of freedom does not relax appreciably during a single collision (although, of course, all modes will thermalize eventually).

To analyze the effect of slowly relaxing degrees of freedom, we consider Eqn. 41. As “hard” internal modes are assumed to relax slowly, we can assume that for those modes $[E_{\text{int}}^{(1)} - E_{\text{int}}^{(2)}]$ is unchanged during a collision.

We consider the general case where some internal modes are “hard” and some are “soft” in Eqn. 66 at the end of this section. However, here we first consider a simpler case, where *all* internal modes are assumed to be hard, because this limit leads an interesting approximation for the thermal conductivity.

If the internal energy is constant during a collision, we have:

$$j_\lambda(0)\Delta j_\lambda \approx \frac{1}{12} \left[-[E_{\text{int}}^{(1)} - E_{\text{int}}^{(2)}]^2 v_{\text{rel}}(0) (v_{\text{rel}}(1) \cos \theta - v_{\text{rel}}(0)) \right. \\ \left. + \frac{mk_B T}{2} v_{\text{rel}}^2(0) [v_{\text{rel}}^2(1) \cos^2 \theta - v_{\text{rel}}^2(0)] \right] \quad (52)$$

In what follows, we consider the limiting case that the internal energy is completely independent of the translational motion before and after the collision³. In that case, we can perform the averaging over internal energies independent of the averaging over translational motion:

$$\begin{aligned}
j_\lambda(0)\Delta j_\lambda &= \frac{1}{12} [[\langle E_{\text{int}}^2 \rangle - \langle E_{\text{int}} \rangle^2] v_{\text{rel}}(0) (v_{\text{rel}}(1) \cos \theta - v_{\text{rel}}(0)) \\
&+ \frac{mk_B T}{2} v_{\text{rel}}^2(0) [v_{\text{rel}}^2(1) \cos^2 \theta - v_{\text{rel}}^2(0)]] \\
&= \frac{1}{12} [[C_V^{\text{int}} k_B T^2] v_{\text{rel}}(0) (v_{\text{rel}}(1) \cos \theta - v_{\text{rel}}(0)) \\
&+ \frac{mk_B T}{3} v_{\text{rel}}^2(0) [(v_{\text{rel}}^2(1) P_2(\cos \theta) - v_{\text{rel}}^2(0)) + (1/2) (v_{\text{rel}}^2(1) - v_{\text{rel}}^2(0))]] \Big] ,
\end{aligned} \tag{53}$$

where we have used the relation between the variance in the internal energy and the heat capacity due to the internal degrees of freedom. Strictly speaking, we could have replaced $v_{\text{rel}}(1)$ in Eqn. 53 by $v_{\text{rel}}(0)$ (because we now assume elastic collisions). We keep the distinction to make it easier to compare the expression for the thermal conductivity with the ones we obtained earlier for the diffusivity and the viscosity. We can now write:

$$\begin{aligned}
\dot{c}_\lambda &= \frac{\Gamma}{12} [[C_V^{\text{int}} k_B T^2] \langle v_{\text{rel}}(0) (v_{\text{rel}}(1) \cos \theta - v_{\text{rel}}(0)) \rangle_c \\
&+ \frac{mk_B T}{3} \langle v_{\text{rel}}^2(0) [(v_{\text{rel}}^2(1) P_2(\cos \theta) - v_{\text{rel}}^2(0)) + (1/2) (v_{\text{rel}}^2(1) - v_{\text{rel}}^2(0))] \rangle_c] \tag{54}
\end{aligned}$$

Using Eqns. 31 and 34, we can write

$$\langle v_{\text{rel}}(0) [v_{\text{rel}}(1) \cos \theta - v_{\text{rel}}(0)] \rangle_c = \frac{12\dot{C}_D}{\Gamma} , \tag{56}$$

$$\langle v_{\text{rel}}^2(0) (v_{\text{rel}}^2(1) P_2(\cos \theta) - v_{\text{rel}}^2(0)) \rangle_c = \frac{60\dot{c}_\eta}{\Gamma m^2} . \tag{57}$$

³Note that this is a stronger assumption than stating that the internal energy does not change during a collision: even if the internal energy is unchanged, the conformation of a molecule may depend on its internal energy, and this would affect the change in the translational velocity during a collision.

Then, using

$$\begin{aligned} D &= -\frac{(k_B T/m)^2}{\dot{C}_D(0+)} , \\ \eta &= -2\rho k_B T \frac{(k_B T)^2}{\dot{c}_\eta(0+)} , \end{aligned}$$

we have

$$\langle v_{\text{rel}}(0) [v_{\text{rel}}(1) \cos \theta - v_{\text{rel}}(0)] \rangle_c = -\frac{12(k_B T/m)^2}{\Gamma D} \quad (58)$$

and

$$\langle v_{\text{rel}}^2(0) (v_{\text{rel}}^2(1) P_2(\cos \theta) - v_{\text{rel}}^2(0)) \rangle_c = -\frac{120\rho(k_B T)^3}{\Gamma m^2 \eta} . \quad (59)$$

we obtain and hence

$$\dot{c}_\lambda = \frac{-\Gamma}{12} \left[[C_V^{\text{int}} k_B T^2] \frac{12(k_B T/m)^2}{\Gamma D} \right. \quad (60)$$

$$\left. + \frac{mk_B T}{3} \left(\frac{120\rho(k_B T)^3}{\Gamma m^2 \eta} + (1/2) \langle v_{\text{rel}}^2(0)(v_{\text{rel}}^2(0) - v_{\text{rel}}^2(1)) \rangle_c \right) \right] \quad (61)$$

The expression for the thermal conductivity then follows from Eqn. 49

$$\begin{aligned} \lambda &= \frac{2\rho}{k_B T^2} \left(\frac{k_B T}{m} \right)^2 \quad (62) \\ &\times \frac{[k_B T^2 C_V^{\text{int}} + 5/2(k_B T)^2]^2}{\frac{1}{12} \left[12[C_V^{\text{int}}/k_B] \frac{(k_B T)^4}{m^2 D} + \frac{mk_B T}{3} \left[\frac{120\rho(k_B T)^3}{m^2 \eta} + (1/2) \langle v_{\text{rel}}^2(0)(v_{\text{rel}}^2(0) - v_{\text{rel}}^2(1)) \rangle_c / \Gamma \right] \right]} \end{aligned}$$

We can simplify this expression, using the fact that we have assumed that the internal energy does not change during a collision:

$$\lambda = \frac{[C_V^{\text{int}}/k_B + 5/2]^2}{\left[\frac{C_V^{\text{int}}/k_B}{2k_B \rho D} + \frac{5m}{3k_B \eta} \right]} = \frac{R\eta}{M} \frac{[C_V^{\text{int}}/k_B + 5/2]^2}{[(C_V^{\text{int}}/k_B) \text{Sc}/2 + (5/3)]} , \quad (63)$$

where $\text{Sc} \equiv \eta/(\rho m D)$ is the Schmidt number, R is the gas constant, and M is the molecular weight (in kg/mol) of the molecules. Eqn. 63 is similar in spirit, but different in form from

the Eucken relation and its many variants². As Eqn. 63 ignores all relaxation of the internal energy, it will typically overestimate the thermal conductivity.

There are many versions of the Eucken relation: all aim to account for the different relaxation rates of translation, rotation and internal vibration. They do so with varying degree of success. Eqn. 63 above is also approximate, and not necessarily particularly accurate. However, it constitutes an interesting limiting case where internal degrees of freedom do not relax at all on the timescales where velocity and stress decay and, as a consequence, it probably yields an upper limit to the true thermal conductivity. A widely used version of the Eucken formula is:^{2,11}

$$\lambda = (R\eta/M) \left[15/4 + Sc \frac{C_V^{int}}{R} \right]. \quad (64)$$

An advantage of expressions such as Eqns. 63 and 64 is that they make it possible to account for strongly quantized internal degrees, as these enter only through the intra-molecular contribution to the heat capacity. We will use Eqn. 64 to estimate λ of n-octane from the computed values of η and ρD , and the tabulated thermal conductivity¹². For atomic gases (no internal degrees of freedom) for which $C_V=(3/2)k_B$, Eqn. 63 reduces to

$$\lambda = \frac{(25/4)}{\frac{5m}{2C_V\eta}} = (5/2)(C_V/m)\eta, \quad (65)$$

which is a well-known result of the Chapman-Enskog theory.

The assumption that the internal energy does not change during a collision is better justified for internal vibrations that are strongly quantized, than for rotations and low-frequency vibrations.

As mentioned above, the assumption that *all* internal modes relax slowly is not essential

and can easily be relaxed, yielding

$$\dot{c}_\lambda = \frac{-\Gamma}{12} \left[C_V^{\text{IH}} k_B T^2 \frac{12(k_B T/m)^2}{\Gamma D} \right. \quad (66)$$

$$\begin{aligned} & + \left\langle -v_{\text{rel}}^2(0) [E_{\text{IS}}^{(1)}(0) - E_{\text{IS}}^{(2)}(0)]^2 \right\rangle_c \\ & + \left\langle v_{\text{rel}}(0) v_{\text{rel}}(1) \cos \theta [E_{\text{IS}}^{(1)}(0) - E_{\text{IS}}^{(2)}(0)] [E_{\text{IS}}^{(1)}(1) - E_{\text{IS}}^{(2)}(1)] \right\rangle_c \\ & + \left. \left\langle \frac{mk_B T}{2} v_{\text{rel}}^2(0) [v_{\text{rel}}^2(1) \cos^2 \theta - v_{\text{rel}}^2(0)] \right\rangle_c \right] \quad (67) \end{aligned}$$

where the superscript IH refers to the hard (slowly relaxing) internal modes, and subscript IS refers to the soft, rapidly relaxing modes. Eqn. 66 can be used in simulations, although we have not done so in this paper.

BGK approximation as a lower bound

To get an estimate of the effect of memory effects that are ignored in the BGK approximation, it is useful to start from our expression for the initial average decay rate of the correlation function, and then consider corrections.

Let us therefore consider the correlation function $C_\alpha(t)$, where J_α stands for particle velocity, shear stress or heat flux.

The BGK approximation implies that we approximate the correlation function $C_\alpha(t)$ with a single exponential

$$C_\alpha(t) \approx C_\alpha(0) e^{-t/\tau}, \quad (68)$$

with

$$1/\tau = \frac{\dot{C}_\alpha(t=0+)}{C_\alpha(0)}; . \quad (69)$$

To analyze the more general case, we make use of the fact that the decay of correlations in a gas at infinite dilution is a Markov process, meaning that the rate of change of a flux $j_\alpha(t)$ depends only on the (complete) set of dynamical variables Y that characterize j_α . We

can then write

$$\dot{j}_\alpha(t) \equiv -Lj_\alpha , \quad (70)$$

which defines the operator L . The formal solution of Eqn. 70 is

$$j_\alpha(t) = e^{-Lt}j_\alpha(0) , \quad (71)$$

and hence

$$C_\alpha(t) = \langle j_\alpha(0)e^{-Lt}j_\alpha(0) \rangle = \langle j_\alpha^2 \rangle \frac{\langle j_\alpha e^{-Lt}j_\alpha \rangle}{\langle j_\alpha^2 \rangle} = \langle j_\alpha^2 \rangle \langle \langle e^{-Lt} \rangle \rangle , \quad (72)$$

where

$$\langle \langle \dots \rangle \rangle \equiv \frac{\langle j_\alpha \dots j_\alpha \rangle}{\langle j_\alpha^2 \rangle} .$$

Of course, the solution of Eqn. 72 would require solving the full kinetic equation, which is the core problem of kinetic theory. But, even without solving Eqn. 72, we can make a general statement about the BGK approximation. Note that, in the language of Eqn 71, the BGK approximation can be written as

$$C_\alpha^{\text{BGK}}(t) = \langle j_\alpha^2 \rangle e^{-\langle \langle L \rangle \rangle t} , \quad (73)$$

where, as before,

$$\langle \langle L \rangle \rangle \equiv \frac{\langle j_\alpha L j_\alpha \rangle}{\langle j_\alpha^2 \rangle} .$$

Note that, as $t \rightarrow 0+$, the full correlation function approaches the BGK expression (as it should):

$$\lim_{t \rightarrow 0+} \langle \langle e^{-Lt} \rangle \rangle = 1 - \langle \langle L \rangle \rangle t = \lim_{t \rightarrow 0+} e^{-\langle \langle L \rangle \rangle t} .$$

Now we can use the fact that the exponential is a convex function. Then Jensen's inequality¹³ applies to Eqns. 72 and 73, implying that

$$\langle \langle e^{-Lt} \rangle \rangle \geq e^{-\langle \langle L \rangle \rangle t} . \quad (74)$$

This inequality implies that the BGK estimate of a transport property must necessarily be a lower bound to the true transport property, provided that the averaging is over a distribution with non-negative weights.

Simulations

We have tested the expression (eqn. 49) for D , η and λ for a number of simple cases where the Chapman-Enskog results are known. In particular, we consider hard spheres and a (truncated) Lennard-Jones model as prototypical examples of particles with no internal degrees of freedom.

After that, we consider one of the few examples of a model of particles with internal degrees of freedom. We chose the rough hard-sphere model, which has been studied by several authors (see refs. 14, 15, 16 and 2).

Hard Spheres

The transport coefficients of a dilute gas of smooth hard spheres were computed using the current approach and compared with the analytical results obtained with the Chapman-Enskog approach, with and without higher-order corrections.

For the simulations, we wrote a (trivial) 2-particle, event-driven hard-sphere MD code. The samples from a Maxwell distribution of relative velocities were drawn using the Box-Muller method. To integrate over the impact parameters between 0 and r_c , we used a 10-point Gauss-Legendre (GL) quadrature. For every impact parameter, we ran 10^5 trajectories. We note that the BGK results are in good agreement with the lowest-order Chapman-Enskog results. We find the same for the case of rough hard spheres (discussed below). This finding suggests that the BGK approximation and the lowest-order Chapman-Enskog expression may be equivalent, at least in some cases. We did not explore this.

The comparison of the numerical (BGK) results are compared with the analytical results

in Table 1

Table 1: Transport coefficients of hard-sphere gas. The column labeled C-E gives the lowest order, Chapman-Enskog analytical results². The column labeled “C-E - higher-order” gives the best available analytical expression¹⁵. The last column presents the simulation results. The error estimates (1σ) are indicated between brackets.

Transport Coefficient	C-E	C-E - higher order	Simulations
ρD	0.2116	0.2149	0.2119(3)
η	0.1763	0.1791	0.175(1)
λ	0.6622	0.6717	0.661(2)

Lennard-Jones gas

To compute the transport coefficients of a dilute LJ gas, we had to perform a large number of binary collisions. In order to make the approach tractable for other users, we used the LAMMPS program package to carry out these simulations. To be precise, we prepared the system as if it were a normal MD run, except that individual collision pairs (initially placed at a distance slightly larger than r_c), were far removed from all other collision pairs. We then created the neighborlist only once and never updated it. For every collision pair ij , the neighbor list contains only one entry. Hence, the simulations are cheap and many collisions (100 000) could be run in parallel. The advantage of this procedure is that it makes the overhead for starting and ending the runs negligible compared with the computational cost of the simulation itself.

The samples from a Maxwell distribution of relative velocities were drawn using the Box-Muller method.

Collision runs were stopped when particles were no longer interacting and moving away from each other. We used a time step $\Delta t = 0.001$ (in reduced units). The Lennard-Jones potential was truncated at a cutoff radius $r_c = 2.5 \sigma$. The force was linearly shifted, such that it vanishes continuously at r_c . As before, we use a 10-point GL quadrature to integrate over impact parameters, and we use 10^5 trajectories per impact parameter.

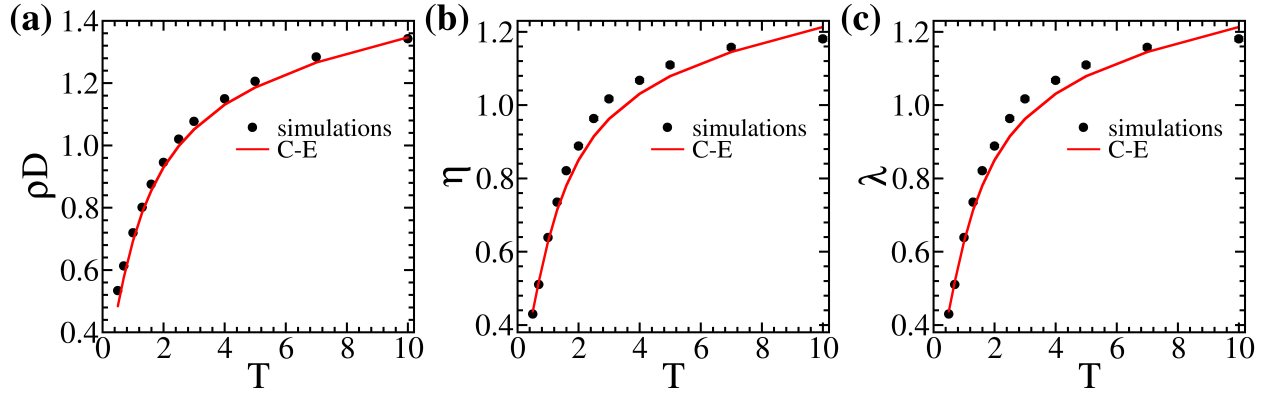


Figure 2: Temperature dependence of (a) the diffusivity D , multiplied with the number density ρ , (b) the viscosity η and (c) the thermal conductivity λ of a dilute Lennard-Jones gas. The drawn curves represent the Chapman-Enskog predictions (see re. 2), the filled circles represent the simulation results obtained using the BGK approximation.

Rough Hard Spheres

The rough hard sphere model is one of the simplest models for a molecule that can exchange both translational and rotational kinetic energy in a collision (the other simple model is the loaded hard sphere model). The model was presumably introduced by G.H. Bryan in 1894 (although the references in ref. 14 and 17 are different and hard to trace). As in the case of hard spheres, we used an event-driven, binary collision code to compute ρD , η and λ using Eqn. 49. The samples from a Maxwell distribution of relative velocities and initial angular momenta were drawn using the Box-Muller method and we used a 10-point GL quadrature to integrate over impact parameters, and we use 10^5 trajectories per impact parameter. For the rough hard-sphere model (RHS), the lowest order Chapman-Enskog approach¹⁴ and higher order expressions^{15,17} are known. Hence, we use this model as a test of our approach for a molecule with internal energy. The results of this comparison are shown in Fig. 3. As is

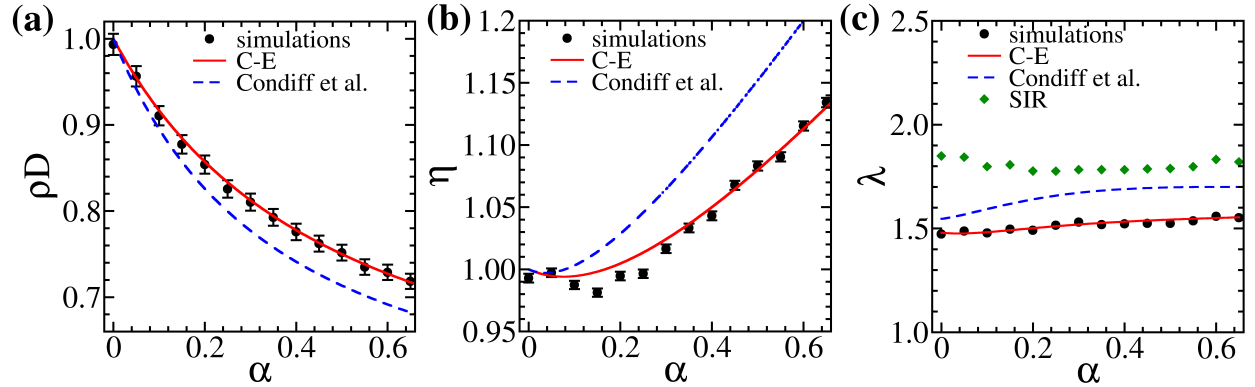


Figure 3: Dependence of the transport coefficients of Rough Hard Spheres, as a function of the dimensionless moment of inertia α , defined as $\alpha \equiv 4I/(m\sigma^2)$, where I is the moment of inertia of the sphere, m its mass, and σ its diameter. All transport coefficients have been divided by the Chapman-Enskog value for hard spheres. Note that the thermal conductivity of rough hard spheres with vanishing moment of inertia is not the same as that of hard spheres, because the latter have no rotational kinetic energy. The figure shows: (a) the diffusivity D , multiplied with the number density ρ , (b) the viscosity η and (c) the thermal conductivity λ . The drawn curves represent the Chapman-Enskog predictions (see 2) and the dashed curves correspond to the higher-order analytical results of ref. 15 - or to be more precise, the corrected expressions given in ref. 17. The filled circles represent the simulation results obtained using the BGK approximation. The filled diamonds in (c) correspond to the Slow Internal Relaxation (SIR) approximation (Eqn. 63).

clear from the figure, our numerical results agree well with the lowest-order Chapman-Enskog results, but may differ by up to 10 % from the more refined analytical expressions. This discrepancy is probably due to the errors introduced by the BGK approximation, although, as we argue below, there may also be problems with the higher-order truncation of the Chapman-Enskog expansion.

Fig. 3(c) also shows the Slow Internal Relaxation (SIR) approximation for λ . The SIR approximation yields a higher estimate for λ than BGK, consistent with the arguments presented in section . The result of ref. 15 for the diffusivity is problematic because we argued in Section that the BGK equation should yield a lower bound to D, η and λ . As is clear from Fig. 3a, the result of ref. 15 for ρD does not satisfy this inequality.

Nitrogen gas

Using the approach described above, we compute ρD , η and λ for a model of nitrogen at temperatures between 233.15 K and 573.15 K. For the sake of comparison with the MD simulations (see below), we used the same 2-center Lennard-Jones model of nitrogen with a rigid bond constraint as used in ref. 8 (be it that we assumed a cutoff distance of 0.8 nm, rather than the somewhat excessive 8 nm mentioned in ref.⁸ . For the trajectory calculations, we used a time step of 10^{-15} s. We used 10 000 collision pairs per run and, to carry out the binary collision calculations efficiently in LAMMPS, we did not update the neighbor list.

The samples from a Maxwell distribution of relative velocities were drawn using the Box-Muller method. We used a short, low-density MD run to generate a sample of randomly oriented, non-interacting molecules with an equilibrated distribution of angular velocities. We used a 10-point GL quadrature to integrate over impact parameters, and we use 10^4 trajectories per impact parameter. The results are shown in figure 4. In the same figure, we also show the corresponding experimental results. The values for η and λ were taken from the reference data of re. 12. The self-diffusion constant of N_2 was reported in ref. 18(to be precise, the data apply to ^{15}N - ^{14}N). The discrepancy between the BGK simulations and the

experiments is not surprising, as we have used a very simple model of nitrogen.

In addition, we performed low-density MD simulations performed using LAMMPS¹⁹. As in ref.,⁸ the number of particles was $N = 1728$, and the time step $\Delta t = 10^{-14}$ s (to facilitate comparison with ref.⁸). To compute the transport properties (in particular, η and λ), rather long simulations were needed. We performed 10 simulations of length 10 ns, excluding 4 ns equilibration time. The transport properties were computed using the Green-Kubo expressions, but in the case of the diffusivity, we also computed D from the mean-square displacement.

In panel (c) we have also indicated the estimate for λ that follows from the approximation given in Eqn. 63, which assumes Slow Internal Relaxation (SIR). Note that, whereas the GK estimate for D and η agree very well with the BGK approximation, the MD results for λ is closer to the SIR approximation. Note that the SIR approximation uses the values for ρD and η listed in the table.

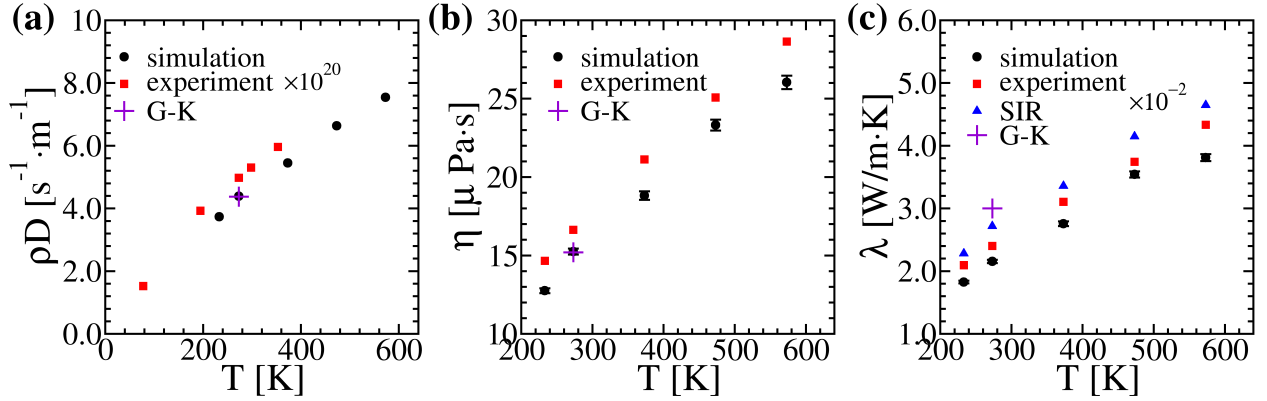


Figure 4: Temperature dependence of (a) the diffusivity D , multiplied with the number density ρ , (b) the viscosity η and (c) the thermal conductivity λ of nitrogen gas (N_2) at infinite dilution. We compare our numerical results with experimental data for nitrogen gas¹² (filled squares). The triangles in panel (c) correspond to the Slow Internal Relaxation (SIR) approximation (Eqn. 63). The crosses indicate the result of brute-force MD simulations for nitrogen at atmospheric pressure and 273 K.

Polyatomic molecules

To illustrate the fact that the present approach can compute quantities that are completely beyond reach for the Chapman-Enskog theory, we give just one example: the transport properties of dilute *n*-octane vapor at $T=300\text{K}$. Again, we used LAMMPS to run many independent binary collisions in parallel.

For the sake of simplicity, we chose a Lennard-Jones-based, united atom force field (NERD)²⁰. We do not expect this force field to be particularly accurate. For the trajectory calculations, we used a time step of 10^{-15} s. We carried out the binary collision calculations on 10 000 pairs in parallel, using LAMMPS without a neighbor list update.

The samples from a Maxwell distribution of relative velocities were drawn using the Box-Muller method. We used a short, low-density NVT-MD run to generate a sample of well equilibrated, non-interacting molecules. We used a 10-point GL quadrature to integrate over impact parameters, and we use 10^4 trajectories per impact parameter. We also computed ρD and η using brute-force MD of 1000 octane molecules (using LAMMPS). In both cases, the BGK results are not statistically different from the MD simulation results. We note, however, that in spite of the fact that we used long MD simulations to compute η (40 ns), the statistical error is large ($\sim 6\%$), as is to be expected. We did not compute λ by MD, because classical simulations do not adequately account for the heat capacity of quantized degrees of freedom. Our estimate for λ , labeled with (*) is based on our numerical results for ρD and η , combined with the corrected Eucken expression 64, using the known value for the internal heat capacity¹².

All results have been collected in Table 2. The experimental data were taken from ref. 12. As can be seen, our estimate for η is in fair agreement with experiment, the agreement for λ is better, but this may be fortuitous. We show this example as an illustration of the fact that, with the present approach, we can produce reasonable estimates for the transport coefficients of poly-atomic gases, based on our knowledge of the molecular force-field.

Table 2: Transport coefficients of n-octane, computed using Eqn. 49, are compared with experiment (where available). Also shown are the estimates for ρD and η from brute-force MD. Our estimate for λ , labeled with (*) is based on our numerical results for ρD and η , combined with the corrected Eucken expression 64, using the known value for the internal heat capacity¹² (see text).

Transport Coefficient		present results	MD simulations	Experiment
ρD	$[\text{s}^{-1}\text{m}^{-1}]$	$3.87(3) \cdot 10^{19}$	$3.30(3) \cdot 10^{19}$	–
η	$[\mu\text{Pa s}]$	$5.73(7)$	$5.2(3)$	5.2
λ	$[\text{W m}^{-1} \text{s}^{-1}]$	$0.0124(*)$	–	0.012

Conclusions

In this paper we proposed a scheme to compute the transport coefficients of dilute molecular gases. The scheme is based on computing the short-time decay of the correlation functions that appear in the relevant Green-Kubo expressions for D , η and λ (the diffusivity, viscosity and thermal conductivity) of the gas. The method that we use is approximate, as it assumes that the correlation functions can be approximated by single exponentials. This approximation, that is similar in spirit to the BGK approximation in kinetic theory, yields results that are in good agreement with the lowest-order Chapman-Enskog expressions (where these are available). However, our results deviate by up to 10% from the results that are obtained by including higher-order terms in the solution of the Boltzmann equation.

For realistic molecular models with internal degrees of freedom, the analytical techniques used to solve the Boltzmann equation become useless. Hence, in these cases, the only alternative is to perform large scale MD simulations on very dilute gases. Such simulations are orders-of-magnitude more time consuming than our simulations, and even then suffer from serious statistical errors, as the relevant correlation functions decay very slowly at low densities. We show that with our approach, we can arrive at reasonable predictions for the transport coefficients of a typical poly-atomic vapor (n-octane). The approach that we propose can easily be extended to mixtures. As we assume that intermolecular interactions have a finite range, the expressions for the transport properties given here are less suited for molecules with long-ranged interactions. However, this limitation can be overcome without

too much trouble.

In principle, the technique that we propose could be made more accurate (e.g. by not making the BGK approximation). Whilst it would be attractive to explore more rigorous approaches to compute gaseous transport properties, we argue that this should be done in a judicious way because otherwise the method could quickly become quite complex and would run the risk of suffering the same fate as the higher-order schemes to solve the Boltzmann equation: these methods are barely used by the non-expert, as *the perfect is the enemy of the good*.

Supporting Information Available

The Supplementary Information describes:

1. How the present approach can be extended to the case of long-ranged intermolecular forces between neutral molecules.
2. How to compute the effect of a collision on the stress tensor.
3. A summary of relevant published analytical expressions for the transport coefficients.
4. a brief description of the expression of other transport coefficients

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Supporting Information:

Using Molecular Simulation to Compute Transport Coefficients of Molecular Gases

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Long-ranged forces

In the main text of the article, we have assumed that the collision integrals can be truncated for impact parameters larger than r_c , the cutoff distance of the potential. Whilst this is often adequate, there may be cases where we wish to account for the effect of long-ranged interactions. Below, we argue that this is, in fact possible, provided that the intermolecular potential decays faster than $1/r$.

First, we note that collision integrals are of the form

$$\begin{aligned}\dot{c}_\alpha &= \rho \langle j_\alpha(0) \Delta j_{\alpha;c} \rangle \\ &= \rho \int dX_{\text{int}} P(X_{\text{int}}) \int_0^\infty \pi db^2 \int_0^\infty dv_{\text{rel}} v_{\text{rel}} P(v_{\text{rel}}) \\ &\equiv \int_0^\infty \pi db^2 \langle \langle v_{\text{rel}} j_\alpha(0) \Delta j_{\alpha;c}(b, v_{\text{rel}}) \rangle \rangle ,\end{aligned}$$

where the double brackets denote averaging over internal degrees of freedom and over relative velocities. We can rewrite this integral as:

$$\dot{c}_\alpha = \int_0^\infty \pi db^2 g(b^2) \frac{\langle \langle v_{\text{rel}} j_\alpha(0) \Delta j_{\alpha;c}(b, v_{\text{rel}}) \rangle \rangle}{g(b^2)} , \quad (\text{S-1})$$

where $g(b^2)$ is a function that is larger than zero, but otherwise arbitrary. We now choose $g(b^2)$ such that it decays to zero as $b^2 \rightarrow \infty$, but not faster than the term between double brackets. The large- b behavior of the term between double brackets depends on the behavior of the intermolecular potential at large distances. We now assume the case of practical interest that the leading r -dependence of the pair potential at large r goes as $v(r) \sim r^{-m}$. Then the intermolecular force decays as $f(r) = \alpha/r^{m+1}$, where α is a measure for the strength of the interaction. For large enough impact parameters, the deflection angle θ of the molecular trajectory becomes small and the quantity $j_\alpha(0) \Delta j_{\alpha;c}(b, v_{\text{rel}})$ scales as $\sin^2 \theta$. In the same limit, we can write

$$\sin \theta \approx \frac{\Delta p}{p_0}$$

where p_0 denotes the original relative momentum, and Δp is its change due to the long-ranged intermolecular forces. To lowest order in θ , we can ignore the fact that the magnitude of the relative momentum changes. Therefore, we can estimate Δp by integrating the force along a straight trajectory:

$$\begin{aligned}
\Delta p &\approx \int_{-\infty}^{+\infty} dt f(r(t)) \times \frac{b}{r(t)} \\
&= \alpha \int_{-\infty}^{+\infty} dt b \left(\frac{1}{b^2 + v_0^2 t^2} \right)^{(m+2)/2} \\
&= \frac{\alpha}{v_0 b^m} \int_{-\infty}^{+\infty} dx \left(\frac{1}{1 + x^2} \right)^{(m+2)/2}, \tag{S-2}
\end{aligned}$$

where $v_0 = p_0/\mu$ and $x \equiv v_0 t/b$. The integral in the last line certainly converges for $m > 1$, which, as we show below, is the range of interest. We are not interested in the numerical value of the integral, just in the fact that it converges. We then have that

$$\sin \theta \approx \frac{\Delta p}{p_0} \sim \frac{1}{p_0^2 b^m}. \tag{S-3}$$

Note that $\sin \theta$ cannot diverge for small p_0 , as $|\sin \theta| \leq 1$. From Eqn. S-3 it follows that $j_\alpha(0)\Delta j_{\alpha;c}(b, v_{\text{rel}})$ scales as b^{-2m} . We can now choose a suitable functional form for $g(b^2)$. Many choices are possible. Here we consider, as an example, the following simple form:

$$\begin{aligned}
g(b^2) &= 1 && \text{for } b^2 \leq r_c^2 \\
&= (r_c/b)^{2\ell} && \text{for } b^2 > r_c^2
\end{aligned} \tag{S-4}$$

We choose $\ell > 1$, such that the integral $\int_0^\infty \pi db^2 g(b^2)$ converges. We do this to ensure that we can write the initial slow of the flux-correlation functions as a product of an effective collision frequency and a change per collisions, as in Eqns. 28, 32 and 35 in the main text.

We note that $\ell \leq m$, because $g(b^2)$ must not decay faster to zero than $j_\alpha(0)\Delta j_{\alpha;c}(b, v_{\text{rel}})$. This condition implies that $m > 1$. This is not a serious constraint if we only consider

uncharged molecules. It is useful to split the integral in Eqn. S-1 in the part for $b < r_c$ and $b \geq r_c$:

$$\begin{aligned} \int_0^\infty \pi db^2 g(b^2) [\dots] &= \int_0^{r_c^2} \pi db^2 [\dots] + \int_{r_c^2}^\infty \pi db^2 \left(\frac{r_c^2}{b^2} \right)^\ell [\dots] \\ &= \int_0^{r_c^2} \pi db^2 [\dots] + \frac{\pi}{\ell-1} \int_0^1 d \left(\frac{r_c^2}{b^2} \right)^{\ell-1} [\dots] , \end{aligned} \quad (\text{S-5})$$

where

$$[\dots] = \frac{\langle \langle v_{\text{rel}} j_\alpha(0) \Delta j_{\alpha;c}(b, v_{\text{rel}}) \rangle \rangle}{g(b^2)} ,$$

which is bounded for $r_c \leq b < \infty$. Both parts of the integral in Eqn. S-5 can be computed numerically by sampling and quadrature. Hence the framework described in the main text can also be applied to long-ranged potentials. It seems plausible that an optimal choice of $g(b^2)$ would be one where the b^2 -dependence of $g(b^2)$ would be the same as for $j_\alpha(0) \Delta j_{\alpha;c}(b, v_{\text{rel}})$. However, we did not investigate this.

Stress correlation

The full stress tensor is a traceless dyadic. $\Sigma = m(\mathbf{v}\mathbf{v} - (1/3)\mathbf{I})$,

$$\Sigma = m \begin{bmatrix} v_x v_x - 1/3 & v_x v_y & v_x v_z \\ v_y v_x & v_y v_y - 1/3 & v_y v_z \\ v_z v_x & v_z v_y & v_z v_z - 1/3 \end{bmatrix} \quad (\text{S-6})$$

First, we need to compute the orientational average $\langle (v_x v_y)^2 \rangle$ (or equivalent). Using polar coordinates, we can write $v_x = v \cos \theta$ and $v_y = v \sin \theta \cos \phi$. Hence

$$\langle (v_x v_y)^2 \rangle = \frac{1}{15} v^4 . \quad (\text{S-7})$$

Rather than working with components, it is better to compute the trace of $\Sigma : \Sigma$, as this quantity is rotationally invariant. Upon orientational averaging

$$\langle (v_x^2 - 1/3)^2 \rangle = \frac{4}{45} v^4. \quad (\text{S-8})$$

The diagonal elements of the orientational average of $\Sigma : \Sigma$ are all equal to

$$\Sigma_{xx}^2 = \langle (v_x^2 - 1/3)^2 \rangle + 2 \langle (v_x v_y)^2 \rangle = \frac{10}{45} v^4 \quad (\text{S-9})$$

or

$$\langle (v_x v_y)^2 \rangle = \frac{1}{10} \text{Tr} \Sigma : \Sigma, \quad (\text{S-10})$$

with $\text{Tr} \Sigma : \Sigma = \frac{2}{3} v^4$.

The advantage of considering the whole matrix Σ is that it transforms as an irreducible tensor of rank 2. Hence, if the post-collisional stress is

$$\Sigma' = m \begin{bmatrix} v'_x v'_x - 1/3 & v'_x v'_y & v'_x v'_z \\ v'_y v'_x & v'_y v'_y - 1/3 & v'_y v'_z \\ v'_z v'_x & v'_z v'_y & v'_z v'_z - 1/3 \end{bmatrix} \quad (\text{S-11})$$

then

$$\text{Tr} \Sigma : \Sigma' = \frac{2}{3} v^2 v'^2 P_2(\cos \theta) \quad (\text{S-12})$$

where θ is the angle between the pre and post collisional velocities.

Using the relation between the trace and the elements of $\Sigma : \Sigma'$, we obtain

$$\langle v_x v_y v'_x v'_y \rangle = \frac{1}{15} v^2 v'^2 P_2(\cos \theta) \quad (\text{S-13})$$

Hence

$$\langle v_x v_y v'_x v'_y \rangle - \langle (v_x v_y)^2 \rangle = \frac{1}{15} \left(v^2 v'^2 P_2(\cos \theta) - v^4 \right), \quad (\text{S-14})$$

which is Eqn. 33 in the main text.

Summary of published analytical expressions for transport coefficients

It is convenient to make the diffusion coefficient D , viscosity η and thermal conductivity λ of rough hard sphere and Lennard-Jones particles dimensionless by dividing them by the corresponding first-order Chapman-Enskog approximations for smooth, hard spheres^{S1}. The smooth hard sphere expressions are:

$$\rho D = \frac{3}{8\sigma^2} \sqrt{\frac{k_B T}{\pi m}} \quad (\text{S-15})$$

$$\eta = \frac{5}{16\sigma^2} \sqrt{\frac{mk_B T}{\pi}} \quad (\text{S-16})$$

$$\lambda = \frac{75}{64\sigma^2} \sqrt{\frac{k_B^3 T}{\pi m}} \quad (\text{S-17})$$

Pidduck,^{S2} evaluated the first-order Chapman-Enskog approximation for rough hard spheres:

$$\rho D = \frac{3}{8\sigma^2} \sqrt{\frac{k_B T}{\pi m}} \frac{1 + \alpha}{1 + 2\alpha} \quad (\text{S-18})$$

$$\eta = \frac{5}{16\sigma^2} \sqrt{\frac{mk_B T}{\pi}} \frac{6(1 + \alpha^2)}{6 + 13\alpha} \quad (\text{S-19})$$

$$\lambda = \frac{75}{64\sigma^2} \sqrt{\frac{k_B^3 T}{\pi m}} \frac{12(1 + \alpha)^2(37 + 151\alpha + 50\alpha^2)}{25(12 + 75\alpha + 101\alpha^2 + 102\alpha^3)} \quad (\text{S-20})$$

where α is the reduced moment inertia, $\alpha = 4I/m\sigma^2$ and I is moment of inertia, of the rough hard sphere. The value of α varies from zero (all mass at the center) to 2/3 (all mass on the surface). A sphere with uniform mass density correspond has $\alpha = 2/5$.

To our knowledge, the highest-order analytical approximation for the transport coefficients of rough hard spheres was given by Condiff, Lu, and Dahler^{S3} (we used the corrected

expression of ref. S4), using a Sonine polynomial expansion. The expression obtained by Condiff *et al.* may differ by up to 10% from the lowest order Chapman-Enskog approximation:

$$\rho D = \frac{3}{8\sigma^2} \sqrt{\frac{k_B T}{\pi m}} \frac{1+\alpha}{1+2\alpha} \times \left[1 + \frac{\pi\alpha(1+\alpha)}{2(1+2\alpha)(5+9\alpha+8\alpha^2)} \right]^{-1} \quad (\text{S-21})$$

$$\eta = \frac{5}{16\sigma^2} \sqrt{\frac{mk_B T}{\pi}} \frac{2(1+\alpha)^2(3+10\alpha)}{6+33\alpha+35\alpha^2} \quad (\text{S-22})$$

$$\lambda = \frac{75}{64\sigma^2} \sqrt{\frac{k_B^3 T}{\pi m}} \frac{4(1+\alpha)(1121+7336\alpha+13449\alpha^2+9490\alpha^3+2000\alpha^4)}{25(116+853\alpha+1707\alpha^2+2266\alpha^3+1360\alpha^4)} \quad (\text{S-23})$$

The first-order Chapman-Enskog approximation for the transport properties of a Lennard-Jones gas is given, for instance, in the book by Chapman and Cowling:^{S1}

$$\rho D = \frac{3}{8\sigma^2} \sqrt{\frac{k_B T}{\pi m}} \frac{1}{W_{12}^{(1)}(1)} \quad (\text{S-24})$$

$$\eta = \frac{5}{16\sigma^2} \sqrt{\frac{mk_B T}{\pi}} \frac{1}{(1/2)W_{12}^{(2)}(2)} \quad (\text{S-25})$$

$$\lambda = \frac{75}{64\sigma^2} \sqrt{\frac{k_B^3 T}{\pi m}} \frac{1}{(1/2)W_{12}^{(2)}(2)}, \quad (\text{S-26})$$

where $W_{12}^{(1)}(1)$ and $W_{12}^{(2)}(2)$ are dimensionless collision integrals^{S5}. The value of these integrals is given in S1 (page 185).

Other transport properties

Bulk viscosity

Using the approach sketched in the text, we can, for instance, obtain an expression for the bulk viscosity, η_B . This quantity is not relevant in the Chapman-Enskog approach for dilute atomic gases, because it vanishes for particles with no internal degrees of freedom. However, for systems with internal degrees of freedom, η_B is finite. The Green-Kubo expression for

η_B in a dilute gas is

$$\eta_B = \frac{1}{9Vk_BT} \int_0^\infty \sum_\alpha \langle J_{\alpha\alpha}(0) J_{\alpha\alpha}(t) \rangle, \quad (\text{S-1})$$

with $\alpha = \{x, y, z\}$. The relevant flux $J_{\alpha\alpha}$ is related to the fluctuation in the trace of the stress tensor, which (for our purposes) only contains kinetic terms.

$$J_{\alpha\alpha} = \sum_{i=1}^N (mv_\alpha^{(i)} v_\alpha^{(i)} - k_B T) . \quad (\text{S-2})$$

Considering, as before, first the rate of change of $J_{\alpha\alpha}$ due to individual collision events, we get (using the same notation as before:

$$\dot{c}_{\eta_B} = \rho \langle \mu^2 v_{\text{rel}}^2(0) \Delta v_{\text{rel}}^2 \rangle = -2\rho \langle \mu v_{\text{rel}}^2(0) \Delta E_{\text{int}}^2 \rangle, \quad (\text{S-3})$$

which shows that only inelastic collisions contribute to the bulk viscosity. In what follows, we shall focus on D , η and λ . Computing η_B for poly-atomic molecules would require a correct description of the collision-induced transitions between different intra-molecular quantum levels.

Thermal Diffusivity

The coefficient for thermal diffusion follows from the cross-correlation function of the diffusive current and the energy flux. In this case, we have to take into account fact that there are (at least) two species. The expression for the \dot{c}_{TD} is

$$\begin{aligned} \dot{c}_{\text{TD}} = \frac{\rho \Delta m}{3M} \left\langle v_{\text{rel}}(0) v_{\text{rel}}(1) \cos \theta \left[\frac{\Delta m}{M} \frac{\mu}{2} v_{\text{rel}}^2(1) + \frac{m_2 \mathcal{E}^{(1)}(1) - m_1 \mathcal{E}^{(2)}(1)}{M} \right] \right. \\ \left. - v_{\text{rel}}^2(0) \left[\frac{\Delta m}{M} \frac{\mu}{2} v_{\text{rel}}^2 + \frac{m_2 \mathcal{E}^{(1)}(1) - m_1 \mathcal{E}^{(2)}(1)}{M} \right] \right\rangle \end{aligned}$$

where we have used the notation $\Delta m \equiv m_2 - m_1$ and $M \equiv m_2 + m_1$ and $\mathcal{E}^{(i)} \equiv E_{\text{int}}^{(i)} - h_i$, where h_i is the partial molar enthalpy of species i .

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